Ay

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 161 625**
A2

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **85105591.3**

(22) Date of filing: **07.05.85**

(51) Int. Cl.⁴: **B 29 C 45/16**, B 29 C 49/22
// B29K67:00, B29K77:00

(30) Priority: **15.05.84 JP 97191/84**

(43) Date of publication of application: **21.11.85**
Bulletin 85/47

(84) Designated Contracting States: **GB IT NL SE**

(71) Applicant: **MITSUBISHI GAS CHEMICAL COMPANY, INC., 5-2, Marunouchi 2-chome Chiyoda-Ku, Tokyo (JP)**

(72) Inventor: **Shimizu, Senzo, 735-25-2, Odake, Odawara-shi Kanagawa-ken (JP)**
Inventor: **Nagano, Mitsuyasu, 2-9-10, Fujimino, Hiratsuka-shi Kanagawa-ken (JP)**
Inventor: **Ishizeki, Tsutomu, 95, Shinomiya, Hiratsuka-shi Kanagawa-ken (JP)**
Inventor: **Momose, Yoshiaki, 1028-5, Kitayana, Hadano-shi Kanagawa-ken (JP)**

(74) Representative: **Kraus, Walter, Dr. et al, Patentanwälte Kraus Weisert & Partner Thomas-Wimmer-Ring 15, D-8000 München 22 (DE)**

(54) **Process for producing multi-layer parison.**

(57) A process for producing a multi-layer parison having a five-layer structure wherein a central layer and two outer layers are made of a thermoplastic resin (resin A) other than a thermoplastic resin (resin B) having gas barrier properties and two intermediate layers held between the central layer and two outer layers are made of the resin B, said process comprising successively injecting the molten resins A and B into a single mold in one injection molding cycle in the order of resin A, resin B and resin A using a molding machine having two injection cylinders for resins A and B under the conditions to meet the following equations (1)–(4),

$V1 \geq V2 \ldots (1)$
$0.5\ cc/sec \leq V2 \leq 20\ cc/sec \ldots (2)$
$0.7 \leq A1/A2 \leq 3.5 \ldots (3)$
$B1/(A1+A2+B1) \leq 0.25 \ldots (4)$

wherein
V1 is an injection rate per parison of the resin A being injected first,
V2 is an injection rate per parison of the resin A being injected last,
A1 is an injection capacity of the resin A being injected first,
A2 is an injection capacity of the resin A being injected last, and
B1 is an injection capacity of the resin B.

EP 0 161 625 A2

Title: Process for producing multi-layer parison

This invention relates to a process for producing a parison having a multi-layer structure, and more specifically to a process for producing a multi-layer parison which is a precursor for obtaining a multi-layer container excellent in transparency, gas barrier properties and mechanical strength.

In recent years, hollow containers using thermoplastic resins have found widespread use as containers of cosmetics, food, beverage, etc. because of such advantages as light weight, safety to burst, etc.

In particular, hollow containers made of polyethylene terephthalate have been rapidly developed by improvement in a biaxial stretching and blow molding technique.

However, biaxially oriented containers made of thermoplastic polyester resins composed mainly of polyethylene terephthalate are not of perfect performance. Above all, in case the content with which the containers are filled is food requiring high gas barrier properties, there are drawbacks that taste of the content is lost for lack of gas barrier properties with respect to oxygen and carbon dioxide gas, and so forth.

In order to remedy these drawbacks, an attempt has been already known to provide a three-layer structure wherein two outer layers are made of a thermoplastic polyester resin and a central layer is made of a m-xylylene group-containing polyamide resin (hereinafter called "MX nylon") being a thermoplastic resin having gas barrier properties (Japanese Patent Publication No. 41181/83 and Japanese Laid-open Patent Applications Nos. 128517/82 and 128520/82). Figure 8 illustrates a sectional view of said three-layer structure.

In the above-described multi-layer containers, the resins having the gas barrier properties, including MX nylon, are inferior in transparency and mechanical

strength to thermoplastic polyester resins. Accordingly, if the content of said resins with the gas barrier properties is too high, the performance of the containers is lost. It is therefore advisable to decrease the content of the resins with the gas barrier properties in such range as to meet the gas barrier performance required.

However, in the above-described known method, it is hard to decrease the content of the resins with the gas barrier properties, above all, MX nylon to less than 30 % by volume. If the content is forcibly decreased, the resin with the gas barrier properties is present only in part of a parison and a layer free of said resin is provided. When said parison is stretched and blow molded into a container, the gas barrier performance is extremely lowered.

In view of the drawbacks of the conventional method, the present inventors made extensive studies and invented a process for producing a five-layer structure wherein a central layer and two outer layers are made of a thermoplastic resin such as a thermoplastic polyester and two intermediate layers held between the central layer and outer layers are made of a thermoplastic resin having gas barrier properties, such as MX-nylon, by which the content of the thermoplastic resin with gas barrier properties can be decreased.

That is, the present invention relates to a process for producing a multi-layer parison having a five-layer structure wherein a central layer and two outer layers are made of a thermoplastic resin (resin A) other than a thermoplastic resin (resin B) having gas barrier properties and two intermediate layers held between the central layer and two outer layers are made of the resin B, said process comprising successively injecting the molten resins A and B into a single mold in one injection molding cycle in the order of resin A, resin B and resin A using a molding machine having two injection cylinders for resins A and B under the conditions to meet the

following equations (1)-(4),

$$V1 \geq V2 \quad \ldots (1)$$
$$0.5 \text{ cc/sec} \leq V2 \leq 20 \text{ cc/sec} \quad \ldots (2)$$
$$0.7 \leq A1/A2 \leq 3.5 \quad \ldots (3)$$
$$B1/(A1 + A2 + B1) \leq 0.25 \quad \ldots (4)$$

wherein

V1 is an injection rate per parison of the resin A being injected first,

V2 is an injection rate per parison of the resin A being injected last,

A1 is an injection capacity of the resin A being injected first,

A2 is an injection capacity of the resin A being injected last, and

B1 is an injection capacity of the resin B.

One injection molding cycle in this invention means a series of steps comprising closing a mold, injecting resins into a cavity of the mold to fill the cavity with said resins, cooling the mold and opening the mold to withdraw a molded article.

This invention is explained hereinafter by referring to the drawings.

Figure 1 is a view illustrating a principle of a device for performing the process of this invention. Figure 2 is a sectional view of a parison obtained in this invention. Figure 3-7 are sectional views of parisons obtained under conditions deviated from those specified in this invention. Figure 8 is a sectional view of a parison obtained according to a conventional method. Figure 9 is a sectional view of a parison obtained with a less amount of the resin B in accordance with the conventional method.

In Figure 1, 1 is a cavity, 2 is a gate, 3 and 3' are cylinders for injecting resins A and B (5, 6: the resins in the mold are shown by an oblique line or solid line yet the resins in the cylinders are not shown in particu-

lar), 4 and 4' are nozzles and 8 is a mold. In this case, a valve by which to switch resin channels may be disposed in a gate. In Figure 1, a portion at which the resins leaving the two injection cylinders meet each other is disposed within the mold but it may be placed without the mold. Figure 1 illustrates a state during the injection where the cavity is not completely filled with the resins, and an unfilled portion 7 remains.

An injection molding method is now concretely explained. The resin A is first injected from the injection cylinder 3 and then the resin B from the injection cylinder 3'. The resin A is finally injected again from the injection cylinder 3 until the cavity is completely filled with the resin, and the pressure is maintained. After cooling is over, the mold is opened and a molded article is withdrawn.

The inside of the cavity is completely filled with the resins for the first time when the last injection of the resin A is finished. At the preceding stage, the unfilled portion remains.

Though amounts of resins injected at the respective stages will be later described, a filling percentage in the cavity at the state where the first injection of the resin A ends is about 30-75 %.

Through the foregoing steps, a parison having a five-layer structure is obtained such that the resin A injected first forms two outer layers, the resin B injected next forms two intermediate layers and the resin A injected finally forms the central layer. Figure 2 illustrates a sectional view of the parison in this case.

However, in order to obtain the parison having substantially the five-layer structure as shown in Figure 2, it is necessary to inject the resins under the limited conditions, which will be explained below by referring to Figures 3-7 showing sectional views of parisons formed under various conditions.

First, as for the injection rates of the resins,

a relationship of $V1 \geqq V2$ shown in equation (1), preferably $V1/V2 \geqq 1.5$ is required. Under the condition of $V1 < V2$, the resin B does not extend in an opening direction on the left as shown in Figure 3 and stays midway. Moreover, the value of V2 has to be 0.5-20 cc/sec shown in equation (2), preferably 1.0-15 cc/sec. Where the value is less than 0.5 cc/sec, the resin is solidified at the gate before terminating the injection to make the inside of the mold unfilled. Where the value exceeds 20 cc/sec, the resin B is all pushed in the opening direction as shown in Figure 4 so that it does not exist in the gate direction.

Next, as for the proportions of the resins being injected, the resin A injected first and the resin A injected last have to meet a relationship of $0.7 \leqq A1/A2 \leqq 3.5$ shown in equation (3), preferably $1 \leqq A1/A2 \leqq 2.5$. With $0.7 > A1/A2$, the resin B is likely to be exposed to the surface in the opening as shown in Figure 5. With $A1/A2 > 3.5$, the resin B does not extend up to the opening as shown in Figure 6. The resins A and B are to meet a relationship of $B1/(A1+A2+B1) \leqq 0.25$ shown in equation (4), preferably $0.03 \leqq B1/(A1+A2+B1) \leqq 0.2$. With $B1/(A1+A2+B1) > 0.25$, the amount of the resin B is too large and likely to stay in the vicinity of the opening.

In the conventional method shown in Figure 8, the resin finally injected is a resin B which partially remains at a gate and is likely to be exposed to the bottom of the stretched container. In this instance, the bottom of the container becomes defective and is easy to break. Moreover, in case of MX nylon, etc. the product is whitened owing to moisture absorption and crystallization, providing poor appearance. The undesirous conditions shown in Figures 5 & 7 are given for the same reasons.

However, according to the present invention, the large amount of the resin A is finally injected as a central layer and the gate portion is therefore completely replaced with the resin A without exposure of said

resin B.

Since the opening and the bottom near the gate of the multi-layer of the parison are not thinned on stretching, the gas barrier properties of the container are not decreased even if the resin B is absent.

In general, the thickness of the multi-layer parison is 2-6 mm, preferably 3-5 mm. The thickness of the multi-layer container biaxially stretched and blow molded is 200-500 μ, preferably 250-450 μ. In this case, considering gas barrier properties, transparency, mechanical strength, etc., a ratio of the resin B based on the overall parison is 25 % or less shown in equation (4), preferably 3-20 %.

Examples of the resin A used in this invention include thermoplastic polyester resins, polyolefin resins, polycarbonates, polyacrylonitrile, polyvinyl chloride and polystyrene. The thermoplastic polyester resins are most preferable.

Examples of the resin B used in this invention, i.e. the thermoplastic resin with the gas barrier properties include MX nylons, ethylene-vinyl acetate copolymer resin saponification products, polyacrylonitrile copolymer resins and polyvinylidene chloride resins. The MX nylons are most preferable.

A combination of the thermoplastic polyester resins, above all, polyethylene terephthalate and MX nylons are most preferable because it is excellent in all of transparency, mechanical strength, injection molding properties and stretch blow molding properties.

Such thermoplastic polyester resins are usually polyesters wherein more than 80 mol%, preferably more than 90 mol% of the acid component is terephthalic acid and more than 80 mol%, preferably more than 90 mol% of the glycol component is ethylene glycol. Examples of the residual acid component are isophthalic acid, diphenylether-4,4'-dicarboxylic acid, naphthalene-1,4 or 2,6-dicarboxylic acid, adipic acid, sebasic acid, decane-

1,10-dicarboxylic acid and hexahydroterephthalic acid. Examples of the residual glycol component are propylene glycol, 1,4-butane diol, neopentyl glycol, diethylene glycol, cyclohexane dimethanol, 2,2-bis(4-hydroxyphenyl)-propane and 2,2-bis(4-hydroxyethoxyphenyl)propane. Further available are polyester resins containing p-oxybenzoic acid, etc. as an oxyacid.

An intrinsic viscosity of these thermoplastic polyester resins is appropriately 0.55 or more, preferably 0.65-1.4. When the intrinsic viscosity is less than 0.55, a multi-layer preform can hardly be obtained in a transparent, amorphous state. In addition, a mechanical strength of the resulting container is not enough.

MX nylons are polymers containing at least 70 mol% of structural units obtained from m-xylylenediamine alone or a xylylenediamine mixture containing m-xylylenediamine and p-xylylenediamine in an amount of less than 30 % of the total amount and an α.ω-aliphatic dicarboxylic acid having 6-10 carbon atoms.

Examples of the polymers include homopolymers such as poly-m-xylylene adipamide, poly-m-xylylene sebacamide and poly-m-xylylene speramide, copolymers such as a m-xylylene/p-xylylene adipamide copolymer, m-xylylene/p-xylylene pyperamide copolymer and m-xylylene/p-xylylene azelamide copolymer, and copolymers of these homopolymer or copolymer components and aliphatic diamines such as hexamethylenediamine, cyclic diamines such as piperazine, aromatic diamines such as p-bis-(2-aminoethyl)benzene, aromatic dicarboxylic acids such as terephthalic acid, lactams such as ε-caprolactam, ω-aminocarboxylic acids such as ω-aminoheptoic acid and aromatic aminocarboxylic acids such as p-aminobenzoic acid.

In these polyesters may be incorporated polymers such as nylon 6, nylon 66, nylon 610 and nylon 11.

A relative viscosity of these MX nylons is suitably at least 1.5, preferably 2.0-4.0.

In this invention, one or both of the resins A

and B may be mixed, if necessary, with coloring agents, ultraviolet absorbers, antistatic agents, antioxidants, lubricants and nucleating agents within such range as not to impair the purpose of this invention.

A multi-layer container produced by heating a multi-layer parison obtained according to the process of this invention to a stretching temperature and biaxially stretching and blow molding the heated parison through expansion with a stretching rod moving axially in a blowing mold and via blowing of a pressurized gas is excellent in gas barrier properties, transparency and mechanical strength.

In this case, the stretching temperature may be approximately the same as that of a parison composed of a thermoplastic polyester resin unit, and a suitable range thereof is 70-130°C. It is advisable to stretch the parison 1-4 times in an axial direction and 2-7 times in a circumferential direction. A more preferable condition is 5-15 times in terms of a stretch ratio for area.

The following Examples and Comparative Examples illustrate the present invention in more detail.

Methods for measuring properties are as follows.

(1) Intrinsic viscosity [η] of a polyester resin:
A phenol/tetrachloroethane (6/4 weight ratio) solvent mixture, a measuring temperature of 30°C

(2) Relative viscosity [η rel.] of a polyamide resin:
1 g of a resin/100 ml of 96 % sulfuric acid, a measuring temperature of 25°C

(3) Haze:
Using NDH-20 manufactured by Nippon Denki Kogyo K. K.

(4) Oxygen permeability:
using OXTRAN 100 manufactured by Modern Control K. K., a temperature of 20°C, a relative humidity of 65 %

(5) Fill point drop test:

A container marked with a fill point is filled with 4 gas volume (3.7 kg/cm, 20°C) of aqueous carbonic acid solution to a given fill point, and the container is sealed. After it is left at 38°C for 24 hours, the distance between the fill point and the liquid level is measured.

(6) Tensile properties:

according to JIS Z-1702

Examples 1-5 and Comparative Examples 1-8:

Using polyethylene terephthalate (hereinafter abbreviated as PET) with an intrinsic viscosity of 0.75 as a thermoplastic polyester resin and poly-m-xylylene adipamide (hereinafter abbreviated as N-MXD 6) with a relative viscosity of 2.1 as MX nylon, a multi-layer parison 30 mm in outer diameter, 120 mm long and 4 mm thick was molded by a two-cylinder injection molding machine.

Common injection conditions are as follows.

Cylinder temperatures:	PET side	275°C
	N-MXD 6 side	265°C
Mold temperature:		20°C
Injection dwell pressure time:		10 sec.
Cooling time:		15 sec.
Injection rate of N-MXD 6:		51.4 cc/sec.

The other injection conditions and the states of parisons obtained are shown in Table 1.

Some of the above obtained parisons were heated with a quartz heater until the surface temperature of the parisons reached 95°C, then transferred into a blowing mold, and biaxially stretched and blow molded using a biaxial stretch blow molding machine under such conditions that a moving speed of a stretching rod was 20 cm/sec and a stretch blowing pressure 20 kg/cm^2. There resulted bottle-shaped hollow multi-layer containers having a total length of 275 mm, an outer diameter of

80 mm and an internal volume of 1000 ml.

The properties of the resulting multi-layer containers are shown in Table 2.

Table 1

	A1 (cc)	A2 (cc)	B1 (cc)	$\frac{A1}{A2}$	$\frac{B1}{A1+A2+B1}$	V1 (cc/sec)	V2 (cc/sec)	$\frac{V1}{V2}$	Results
Ex. 1	15.7	13.7	6.3	1.1	0.18	38.8	10.0	3.9	Fig. 1
Ex. 2	17.6	14.7	3.1	1.2	0.09	38.8	10.0	3.9	"
Ex. 3	16.7	15.7	1.6	1.1	0.05	38.8	10.0	3.9	"
Ex. 4	17.6	14.7	3.1	1.2	0.09	38.8	1.5	25.9	"
Ex. 5	16.7	15.7	1.6	1.1	0.05	38.8	14.0	2.8	"
Comp. Ex. 1	36.3	-	-	-	-	30.2	-	-	Single layer
Comp. Ex. 2	15.7	4.9	13.9	3.2	0.40	30.2	10.0	3.0	Fig. 8
Comp. Ex. 3	24.5	4.9	6.3	5.0	0.18	30.2	10.0	3.0	Fig. 9
Comp. Ex. 4	17.6	14.7	3.1	1.2	0.09	19.9	38.8	0.5	Fig. 3
Comp. Ex. 5	17.6	14.7	3.1	1.2	0.09	38.8	24.2	1.6	Fig. 4
Comp. Ex. 6	9.8	19.6	3.1	0.5	0.09	38.8	10.0	3.9	Fig. 5
Comp. Ex. 7	23.5	5.9	3.1	4.0	0.09	38.8	10.0	3.9	Fig. 6
Comp. Ex. 8	12.7	14.7	9.5	0.9	0.26	38.8	10.0	3.9	Fig. 7

Table 2

	Haze (%)	Amount of decrease in oxygen permeability (cc/bottle.day.atm)	Fill point drop (mm)	Tensile yield strength (kgf/cm^2)	Tensile strength at break (kgf/cm^2)
Ex. 1	6.2	0.04	14	1400	1420
Ex. 2	3.0	0.07	13	1540	1570
Ex. 3	2.2	0.09	10	1560	1620
Comp. Ex. 1	3.0	0.30	9	1600	1690
Comp. Ex. 2	10.1	0.03	20	1230	1230

What we claim is:

1. A process for producing a multi-layer parison having a five-layer structure wherein a central layer and two outer layers are made of a thermoplastic resin (resin A) other than a thermoplastic resin (resin B) having gas barrier properties and two intermediate layers held between the central layer and two outer layers are made of the resin B, said process comprising successively injecting the molten resins A and B into a single mold in one injection molding cycle in the order of resin A, resin B and resin A using a molding machine having two injection cylinders for resins A and B under the conditions to meet the following equations (1)-(4),

$$V1 \geqq V2 \quad \ldots (1)$$

$$0.5 \text{ cc/sec} \leqq V2 \leqq 20 \text{ cc/sec} \quad \ldots (2)$$

$$0.7 \leqq A1/A2 \leqq 3.5 \quad \ldots (3)$$

$$B1/(A1+A2+B1) \leqq 0.25 \quad \ldots (4)$$

wherein

V1 is an injection rate per parison of the resin A being injected first,

V2 is an injection rate per parison of the resin A being injected last,

A1 is an injection capacity of the resin A being injected first,

A2 is an injection capacity of the resin A being injected last, and

B1 is an injection capacity of the resin B.

2. The process of claim 1 wherein the resin A is a thermoplastic polyester resin and the resin B is a m-xylylene group-containing polyamide resin.

Fig. 1

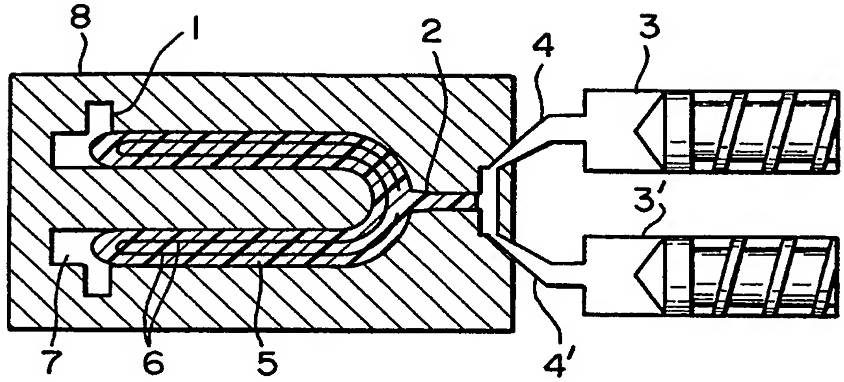

Fig. 2

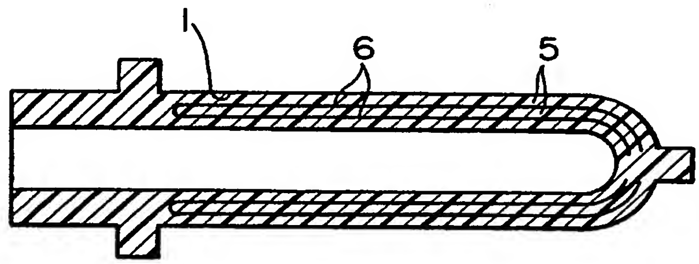

Fig. 3

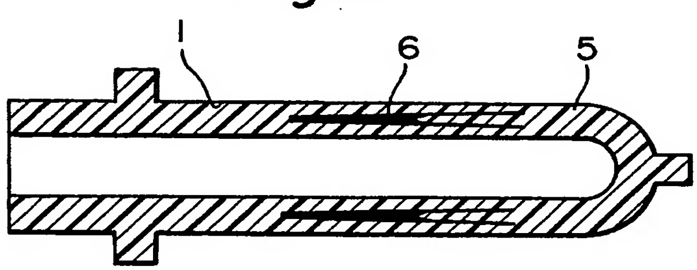

Fig. 4

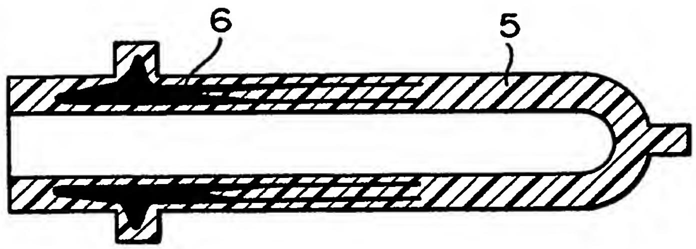

Fig. 5

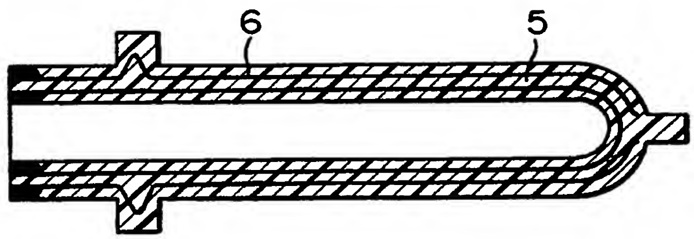

Fig. 6

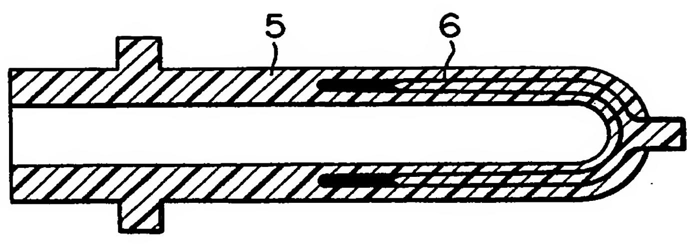

Fig. 7

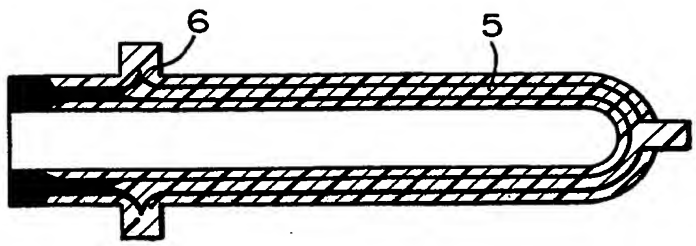

Fig. 8

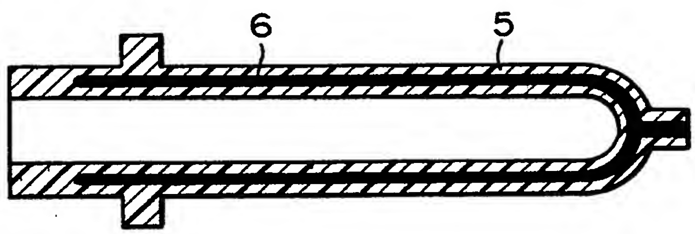

Fig. 9

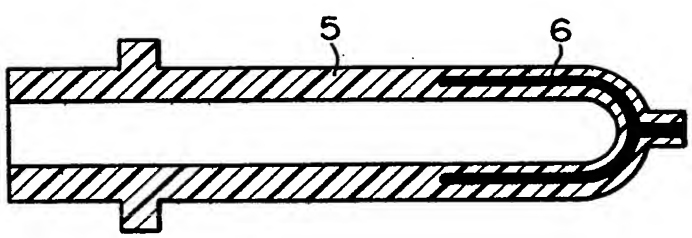

Fig. 10

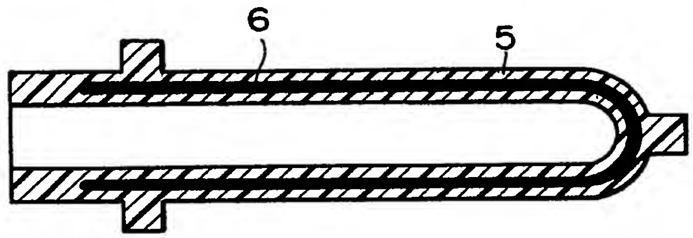

Fig. 11